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(54) **A curable composition.**

(57) A curable composition which comprises (A) an oxyalkylene polymer having a silicon-containing group(s) that has a hydroxy group(s) and/or a hydrolyzable group(s) bonded to the silicon atom(s), and can be crosslinked by forming siloxane bonds, and (B) hollow microspheres of vinylidene chloride polymer having a true specific gravity of 1 g/cm<sup>3</sup> or less.

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The present invention relates to a curable composition that comprises an oxyalkylene polymer having a silicon-containing group(s) that has a hydroxy group(s) and/or a hydrolyzable group(s) bonded to a silicon atom(s), and can be crosslinked by forming siloxane bond.

An oxyalkylene polymer that comprises a silicon-containing group(s) having a hydroxy group(s) and/or a hydrolyzing group(s) bonded to a silicon atom(s), (to be referred to as a reactive silicon group(s) hereinafter) that can be crosslinked by forming siloxane bonds disclosed, for example, in Japanese Patent Publication, No. 52-72998 and USP. 3,971,751.

Its typical example is a polymer represented by the general formula:

$X''_3 \text{ Si} - (\text{oxypropylene polymer}) - \text{Si}X''_3$  [where  $X''$  represents a hydrolyzable group such as methoxy group].

An oxyalkylene polymer having a reactive silicon group(s) cures by forming siloxane bonds (Si-O-Si) between polymers by the action of moisture at room temperature like room temperature curable silicone rubber, and produces a rubber-like cured substance. This cured substance is so excellent in elongation properties, strength and adhesiveness that it is used as sealants, adhesives and such.

This polymer may be used, for the purpose of lowering costs, in a composition to be mixed with a filler.

Addition of a filler, however, has been problematic: it increases the weight of the cured substance, and it does not lower the cost as expected.

Although it has been suggested that addition of glass microspheres may be beneficial, the resulting cured material often has its elastic properties impaired, i.e., reduced elongation properties and increased tensile modulus.

It has been disclosed in Japanese Patent Publication, No. 63-191856 that organic hollow microspheres of a vinylidene chloride polymer are added to a polyurethane substrate to improve the adhesiveness to the substrate.

The present inventors found that these organic hollow microspheres are capable of affording a lightweight, highly-filled cured substance without degrading the physical characteristics such as elongation properties, and of reducing the costs greatly.

The present invention provides a curable composition which comprises:

(A) an oxyalkylene polymer having a silicon containing group(s) that has hydroxy and/or hydrolyzable group(s) bonded to the silicon atom and can be crosslinked by forming siloxane bonds, and

(B) hollow microspheres of a vinylidene chloride polymer having a true specific gravity of 1 g/cm<sup>3</sup> or less.

The oxyalkylene polymer having at least one reactive silicon group which can be used in the present invention (hereinafter referred to as an oxyalkylene polymer (A)) is a known polymer as disclosed in Japanese Patent Publication, Nos. 45-36319, 46-12154, 49-32673 and 52-72998, and Japanese Patent Disclosure, Nos. 50-156599, 51-73561, 54-6096, 55-82123, 55-123620, 55-125121, 55-131022, 55-135135 and 55-137129, and U.S. Patent No. 3,971,751.

The molecular chain of the oxyalkylene polymer (A) essentially consists of the repeating units as represented by the general formula:

$-R^1-O-$

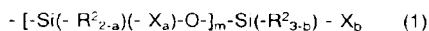
where  $R^1$  represents a substituted or unsubstituted divalent hydrocarbon group having 1 to 12 carbon atoms

The main chain of the oxyalkylene polymer may consist only of the repeating units represented by the general formula:

$-R^1-O-$ , or it may contain, in addition, other repeating units. When it contains other repeating units, the repeating unit represented by the formula:  $-R^1-O-$  should preferably constitute 60% (weight %, unless otherwise stated) or more, or more preferably 80% or more based on the whole weight of the polymer.

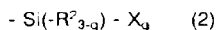
$R^1$  in the formula  $-R^1-O-$  is preferably a substituted or unsubstituted divalent aliphatic hydrocarbon group having 2 to 5 carbon atoms, especially, an aliphatic hydrocarbon group having 3 or 4 carbon atoms. Examples of  $R^1$  include  $-\text{CH}(\text{CH}_3)\text{CH}_2-$ ,  $-\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2-$ ,  $-\text{C}(\text{CH}_3)_2\text{CH}_2-$  and  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$ , with  $-\text{CH}(\text{CH}_3)\text{CH}_2-$  being preferred. The molecular chain of said oxyalkylene polymer (A) may comprise either one or more than one kind of the repeating unit of the formula  $-R^1-O-$ .

The reactive silicon group in the oxyalkylene polymer (A) is a well-known functional group and is characterized by crosslinkability even at room temperature. Typical example of the reactive silicon group is a group represented by the following formula (1).



Wherein R<sup>2</sup> is a monovalent organic group having 1-40 carbon atoms, and when two or more R<sup>2</sup> are present, they may be the same or different, X is a hydroxy group or a hydrolyzable group, and when two or more Xs are present, they may be same or different; a is either 0, 1 or 2; b, either 0, 1, 2 or 3; and the sum of a and b ≥ 1; m is 0 or an integer of 1 to 19, and when m is two or more, a's in  $[-\text{Si}(\text{R}^{2\text{a}})_2(\text{X}_\text{a})\text{O}]_m$  are not necessarily the same.

Among the reactive silicon groups represented by the formula (1), from the viewpoint of economy, a group represented by the formula:



where  $R^2$  represents the same as described above, and  $q$  is either 1, 2 or 3, is preferred.

Specific examples of a possible hydrolyzable group X in the formula (1), include a halogen atom, a hydrogen atom, an alkoxy, an acyloxy, a ketoximate, an amino, an amide, an aminoxy, a mercapto, and an alkenyloxy group. Alkoxy groups such as methoxy and ethoxy group are preferred because they are mildly hydrolyzed and easily handled.

Further, typical examples of R<sup>2</sup> in the formula (1) include a substituted or unsubstituted hydrocarbon group having 1-40 carbon atoms and a triorganosiloxy group. Specific examples of R<sup>2</sup> include alkyl groups such as methyl or ethyl groups; cycloalkyl groups such as a cyclohexyl group; aryl groups such as a phenyl group; aralkyl groups such as a benzyl group; and triorganosiloxy groups represented by the formula, (R<sup>1</sup>)<sub>3</sub>SiO - wherein R<sup>1</sup> is an organic group having 1-20 carbon atoms, and three R<sup>1</sup> groups are not necessarily the same such as a trimethylsiloxy group. Among these groups a methyl group is particularly preferred.

The oxyalkylene polymer (A) should contain at least one reactive silicon group. For obtaining a sufficient curability, however, it is desirable that the polymer (A) contains at least 1.1, more preferably from 1.5 to 4 reactive silicon groups. Further, the reactive silicon group should be preferably located at the terminal of the molecular chain of the oxyalkylene polymer (A).

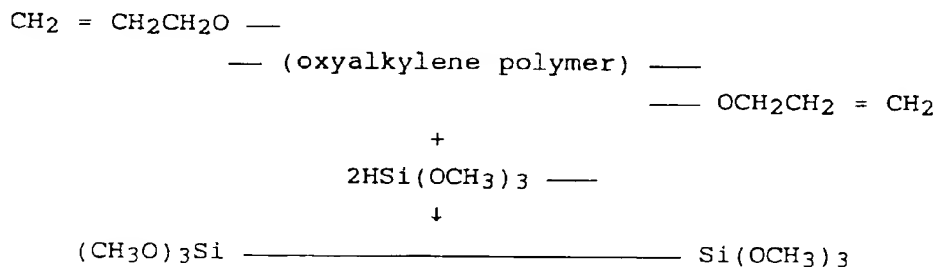
The number average molecular weight of the oxyalkylene polymer (A) should be preferably from 3,000 to 50,000 or more preferably from 5,000 to 30,000. The oxyalkylene polymer (A) may be used alone or in a combination of two or more analogues.

30 The oxyalkylene polymer (A) can be produced by various procedures. One example of the procedures comprises reacting an oxyalkylene polymer having a certain functional group (designated as Y group) with a compound having a functional group capable of reacting with the Y group and a reactive silicon group, to introduce the reactive silicon group into the oxyalkylene polymer.

Specific examples are as follows.

35 (i) a procedure wherein an oxyalkylene polymer having an unsaturated group and a hydroxysilane compound having a hydrolyzable group such as  $\text{HSi}(\text{OCH}_3)_3$  are allowed to react (hydrosilylation) under the catalytic influence of, for example, a Group VIII transition metal compound.

(Example of the reaction)

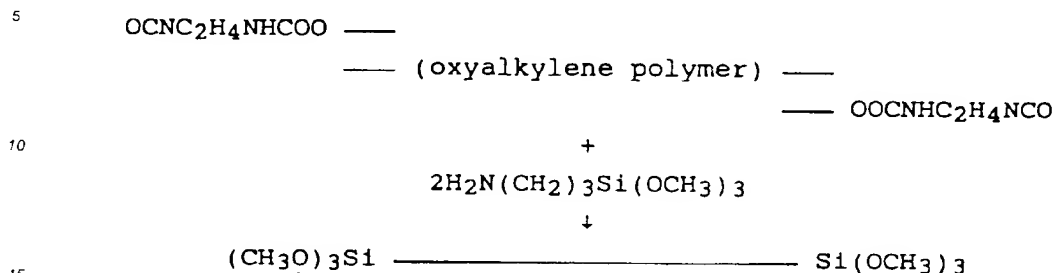


55 (ii) a second procedure wherein an oxyalkylene polymer having an unsaturated group, and a compound having a mercapto group and a reactive silicon group such as  $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$  are allowed to react by an addition reaction, and

(iii) a third procedure wherein an oxyalkylene polymer having an isocyanate group, and a compound having an active hydrogen group and a reactive silicon group such as  $H_2N(CH_2)_3Si(OCH_3)_3$  are allowed

to react.

(Example of the reaction)



(iv) a fourth procedure wherein an oxyalkylene polymer having a hydroxy group, and a compound having an isocyanate group and a reactive silicon group such as  $\text{OCN}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ , are allowed to react.

Of those procedures, the one wherein an oxyalkylene polymer having an unsaturated group and a hydrosilane compound are allowed to react is frequently used. The oxyalkylene polymer having an unsaturated group, can be obtained by introducing the unsaturated group into the polymer, utilizing the hydroxy group in that polymer, as disclosed in Japanese Patent Disclosure No. 54-6097 and No. 3-72527.

The oxyalkylene polymer (A) to be used in the present invention is not limited to those obtained by said procedures, but the polymer obtained by any other procedures can be used. The oxyalkylene polymer (A) in this invention also includes a polymer that is obtained by polymerizing polymerizable monomers such as vinyl monomers in the presence of an oxyalkylene polymer (A), or a polymer that is obtained by polymerizing polymerizable monomers in the presence of an oxyalkylene polymer having a hydroxy group and then by introducing a reactive silicon group into it.

The hollow microspheres (balloons) means hollow bodies composed of inorganic or organic materials having each a diameter of 1 mm or less, preferably of 500  $\mu\text{m}$  or less, as described, for example, in "Modern Techniques for Functional fillers (Kinosei fira no saishin-gijutsu)" (CMC).

In the present invention, are used hollow micro spheres of a vinylidene chloride polymer that are a sort of organic hollow microspheres. By using these hollow microspheres the tensile modulus of the cured product can be improved (lower modulus of cured product can be achieved) without lowering the elongation properties.

The vinylidene chloride polymer as a material of the hollow microspheres may be a homopolymer of vinylidene chloride or a copolymer with, for example acrylonitrile or others. When a copolymer is used, the amount of the vinylidene chloride unit should preferably be 50 weight % or more of the polymer. Hollow microspheres having their outer surface coated with, e.g., a thermosetting resin may be used.

The hollow microspheres used in this invention should have a true specific gravity of 1  $\text{g}/\text{cm}^3$  or less, preferably of 0.5  $\text{g}/\text{cm}^3$  or less, more preferably 0.1  $\text{g}/\text{cm}^3$  or less, or particularly preferably 0.05  $\text{g}/\text{cm}^3$  or less.

Examples of the hollow microspheres to be used in the present invention include Saran microspheres (Dow Chemical Co.) called Saran balloons, Exban cells (Japan Fillite), and Matsumoto microspheres (Matsumoto Oil Pharmaceutical).

In the present invention, the hollow microspheres of a vinylidene chloride polymer may be used in combination with other hollow microspheres made of inorganic or organic materials.

The inorganic hollow microspheres can be classified into silicate based spheres and nonsilicate spheres: the former includes silas balloons (hollow microspheres made of volcanic ash), pearlite, glass balloons, silica balloons or fly ash balloons, and the latter includes alumina balloons, zirconia balloons or carbon balloons.

The organic hollow microspheres can be classified into thermosetting spheres and thermoplastic spheres: the former include phenolic balloons, epoxy balloons or urea balloons, and the latter include polystyrene balloons, polymethacrylate balloons, polyvinylalcohol balloons or styrene-acrylate polymer balloons. Further, certain thermoplastic spheres have their surface coated with thermosetting resins. Crosslinked thermoplastic sphere may be used. The composition of the present invention may be prepared by formulating the oxyalkylene polymer (A) and a precursor of hollow microspheres, for example micro-

spheres containing a foaming agent, and then foaming the spheres to afford hollow spheres.

The hollow micro spheres other than the one made of a vinylidene chloride polymer are available in the market under various trade names. For example, for silas balloons, Winlite (Ijichi Chemical) is marketed. For glass balloons, Micro balloon (Emerson & Cuming), Glass Bubbles (3M), Celamic glass modules (Pittsburgh Corning Corp.), and Cell-star (Asahi Glass) are put to sale. For silica balloons, Q-cel (Philadelphia Quartz Co.) is sold. For fly ash balloons, Corospheres (PFA Marketing Ltd.) and Fillite (Fillite U.S.A. Inc.) are commercialized.

For alumina balloons, BW (Showa Denko) is available, while for zirconia balloons, Hollow zirconium spheres (Zircoa) can be purchased. For carbon balloons, Kureka Spheres (Kureha Chemicals) and Carbo spheres (General Technologies Corp.) are marketed.

For phenol balloons, Phenolic microballoons (UCC), for epoxy balloon, Eccospheres EP (Emerson & Cuming), and for urea balloons, ECCO Spheres VF-0 (Emerson & Cuming) is sold.

For polystyrene balloons, Dylite expandable polystyrene (Arco Polymers Inc.) and Expandable polystyrene beads (BASF Wyandote Corp.) are sold. For crosslinkable styrene-acrylate balloons, SX863(P) (Japan Synthetic Rubber) is available.

The hollow micro spheres are usually added in an amount of 0.01-100 parts (based on weight unless otherwise stated), preferably 0.1-50 parts, or more preferably 0.3-40 parts per 100 parts of the oxyalkylene polymer (A).

The compositions of the present invention may further contain a silanol condensation catalyst, a plasticizer, a filler besides the hollow microspheres, or other additives.

For curing the composition of the present invention, a silanol condensation catalyst (a curing catalyst) may be used. Specific examples of silanol condensation catalysts are: titanate esters such as tetrabutyl titanate or tetrapropyl titanate tin carboxylic acid salts such as dibutyl tin dilaurate, dibutyl tin maleate, dibutyl tin diacetate, tin octylate or tin naphthenate the reaction products from dibutyl tin oxide and phthalate esters: dibutyl tin acetylacetonate; organic aluminum compounds such as aluminum trisacetyl acetate, aluminum triethyl acetoacetate or diisopropoxy aluminum ethyl acetoacetate; chelate compounds such as zirconium tetraacetyl acetate or titanium tetraacetyl acetate; lead octylate; amine compounds such as butyl amine, octyl amine, dibutyl amine, monoethanol amine, diethanol amine, triethanol amine, diethylene triamine, triethylene tetramine, oleyl amine, cyclohexyl amine, benzyl amine, diethylaminopropyl amine, xylylene diamine, triethylene diamine, guanidine, diphenyl guanidine, 2, 4, 6-tris (dimethyl aminomethyl) phenol, morpholine, N-methyl morpholine, 2-ethyl-4-methylimidazole, 1, 8-diazabicyclo (5, 4, 0) undecene-7 (DBU), or the salts of those amine compounds and carboxylic acids and others; low molecular-weight polyamide resins obtained by the reaction of excess polyamines with polybasic acids; the reaction products from excess polyamines and epoxy compounds; and silan coupling agents having amino groups such as  $\gamma$ -aminopropyltrimethoxysilan or N-( $\beta$ -aminoethyl) aminopropylmethyl dimethoxysilan. Besides, known silanol condensation catalysts can also be used. These catalysts may be used alone or in combination of two or more.

When said silanol condensation catalysts are used, they are added in an amount preferably of from 0.1 to 20 weight parts, or more preferably from 1 to 10 weight parts per 100 parts of the oxyalkylene polymer (A). If the amount of the silanol condensation catalyst is too small relative to the amount of the oxyalkylene polymer (A), the curing rate becomes slow and the curing reaction does not proceed to a sufficient degree. On the other hand, if the amount of the silanol condensation catalyst is too high, local heat generation or foaming during curing impairs the quality of the cured product.

The compositions of the present invention can be further modified by adding thereto various fillers. Examples of the fillers include reinforcing fillers such as fumed silica, precipitating silica, silicic anhydride, hydrated silicate and carbon black; fillers such as calcium carbonate, magnesium carbonate, diatomaceous earth, calcined clay, clay, talc, titanium oxide, bentonite, organic bentonite, ferric oxide, zinc oxide and activated zinc powder; and fibrous fillers such as glass fiber and filament.

When a high strength cured product is desired fillers such as fumed silica, precipitating silica, silicic anhydride, hydrated silica, carbon black, surface-treated fine powder of calcium carbonate, calcined clay, clay and activated zinc powder are preferably added in an amount of from 1 to 200 parts per 100 parts of the oxyalkylene polymer (A). When a product having a low strength and great elongation properties is desired, fillers such as titanium oxide, calcium carbonate, magnesium carbonate, talc, ferric oxide or zinc oxide are preferably added in an amount of from 5 to 200 parts per 100 parts of the oxyalkylene polymer (A). Needless to say, those fillers can be used alone or in combination of two or more. Particularly when the compositions of the present invention comprise a reinforcing filler, light-weight cured product can be obtained, retaining the mechanical strength of the cured product as compared with that of the composition containing solely a reinforcing filler.

The composition of the present invention can contain a plasticizer to improve elongation properties of the cured product or to enable to incorporate a larger amount of fillers. E. g., the following plasticizers may be used alone or in combination of two or more: phthalate esters such as dioctyl phthalate, dibutyl phthalate or butylbenzyl phthalate; aliphatic dibasic acid esters such as dioctyl adipate, isodecyl succinate or dibutyl sebacate; glycol esters such as diethylene glycol dibenzoate, or pentaerythritol ester; aliphatic esters such as butyl oleate or methyl acetyl ricinoleate; phosphate esters such as tricresyl phosphate, trioctyl phosphate or octyldiphenyl phosphate; epoxy plasticizers such as epoxydized soybean oil or benzyl epoxy stearate polyester plasticizers such as polyesters resulting from dibasic acids and divalent alcohols; polyethers such as polypropylene glycol and its derivatives; polystyrenes such as poly- $\alpha$ -methylstyrene or polystyrene; and other plasticizers such as polybutadiene, butadiene-acrylonitrile copolymer, polychloroprene, polyisoprene, polybutene or chlorinated paraffin. Plasticizers are usually used in an amount of from 0 to 150 parts per 100 parts of the oxyalkylene polymer (A).

In addition to the fillers, plasticizers and condensation catalysts, various additives including adhesion imparting agents such as phenol resin or epoxy resin, pigments, antioxidants, or UV-absorbing agents may be added as needed.

The composition of the present invention can be formulated to either a one pack type or a two pack type composition. When a two pack type composition is prepared, it should be divided into two components, for example: one component comprising the oxyalkylene polymer (A), filler and plasticizer and the other, a filler, plasticizer and condensation catalyst. The two components are mixed immediately before use. When a one pack type composition is prepared the oxyalkylene polymer (A), filler, plasticizer and condensation catalyst are thoroughly removed of moisture and dried, mixed together under the exclusion of water, and preserved in a container like a cartridge, then the content is ready to be used as a one-pack type composition of good storage stability.

The compositions of this invention are particularly useful as a one or two pack type elastic sealant, and can be used as a sealing agent for buildings, ships, automobiles, roads and others. Further, alone or with a primer, they can be applied to a wide variety of substrates such as glass, china, lumber, metals or resin molds so that they can be used as a composition for various types of sealing or adhesive agents. Furthermore, they may be used for food packing materials, injection rubber materials, or molding materials.

For further demonstrating this invention, explanation will be given by following Examples.

#### Synthetic Example

800 g of an oxypropylene polymer which has allylether groups introduced into 97% of all the terminals, and having an average molecular weight of 8,000 was placed in a pressure reactor with a stirrer, to which was added 19 g of methyldimethoxy silane, followed by the addition of 0.34 ml of chloroplatinic acid catalyst solution (8.9 g of  $H_2 \cdot PtCl_6 \cdot 6H_2O$  dissolved in 18 ml of isopropyl alcohol and 160 ml of tetrahydrofuran). The mixture was allowed to react at 80°C for 6 hours.

The hydrosilyl group of methyldimethoxy silane in the reaction solution was determined by IR spectrum analysis and it was found that substantially no methyldimethoxy silane was present. The amount of reactive silicon groups was determined by NMR, and it was found that the resulting polyoxypropylene had about 1.7 reactive silicon groups  $(CH_3O)_2(CH_3)SiCH_2CH_2CH_2O$  per one molecule at its molecular terminals.

#### Examples 1 - 3 and Comparative Examples 1 - 5

100 parts (based on weight unless otherwise stated hereinafter) of the polymer synthesized as described in the Synthetic Example, and 60 parts of calcium carbonate (Shiraishi Industrial Co., Hakuenka CC-R) are mixed thoroughly with a three-roll paint mill. To the mixture was added 0-10 parts of hollow microspheres and 1 part of dibutyl tin diacetylacetonate (Nitto Chemical, U-220) as a condensation catalyst, and they were kneaded by hand to produce a sheet of 3 mm thick. The sheet was allowed to cure at 23°C for 3 days, then at 50°C for 4 days. The sheet then was cut into pieces with a JIS #3 dumbbell in accordance with JIS K 6301, and the test piece was submitted to the tensile strength test using autography at a rate of 200 mm/min. The result is shown in Table 1.

In this Table, the balloon A are hollow microspheres of a vinylidene chloride polymer (Matsumoto Microspheres F80ED produced by Matsumoto Oil Pharmaceutical), the balloon B are hollow microspheres of phenolic resin (Ucarphenolic microballoons BJO-0930 by Union carbide), and the balloon C are hollow microspheres of glass (Q-coll #300 by Asahi Glass Co).

M100, TB and EB in table 1 represent modulus at 100% elongation, tensile strength at break and elongation at break, respectively.

Table 1

Examples	Balloon	True specific gravity of balloon	Weight parts	Volume ratio between calcium carbonate and balloons	Tensile strength test		
					M100 kg/cm <sup>2</sup>	TB kg/cm <sup>2</sup>	EB %
Examples 1	A	0.024	0.3	1/0.5	3.9	7.9	420
" 2	A	0.024	0.6	1/1	3.7	6.9	425
" 3	A	0.024	1.2	1/2	3.4	5.5	395
Comparative Examples 1	B	0.23	5	1/1	4.5	6.4	420
" 2	B	0.23	10	1/2	4.8	5.1	320
" 3	C	0.21	5	1/1	4.8	8.2	335
" 4	C	0.21	10	1/2	5.6	8.0	265
" 5	Non	--	--	--	4.1	8.0	435

As is evident from this table 1, when hollow micro spheres (balloons) of a vinylidene chloride polymer is used as a filler, a light-weight cured product having improved (low) modulus can be obtained without degrading its elongation properties.

Three compositions containing further 100 parts of dioctyl phthalate were prepared through similar procedure as examples 1 to 3.

The cured product of the resulting composition was found to have excellent tensile properties as well.

Claims

1. A curable composition which comprises (A) an oxyalkylene polymer having a silicon-containing group-  
5 (s) that has a hydroxy group(s) and/or a hydrolyzable group(s) bonded to the silicon atom(s), and can  
be crosslinked by forming siloxane bonds, and (B) hollow microspheres of a vinylidene chloride  
polymer having a true specific gravity of 1 g/cm<sup>3</sup> or less.

2. A curable composition according to claim 1, which comprises further a reinforcing filler.

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European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 92 11 0673

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A,D	US-A-3 971 751 (KATSUHIKOMO ISAYAMA ET AL) * The Whole Document * ---	1	C08G65/32 C08J9/32 C08L71/02 C08K7/22
A	DE-A-3 100 746 (DIETZ A. ET AL) * claim 1 * ---	1	
A	DATABASE WPIL Derwent Publications Ltd., London, GB; AN 89-275838(38) & JP-A-1 202 683 (KAGAKU GIJUTSU-CHO KINZ) 15 August 1989 * abstract * ---	1,2	
A	EP-A-0 264 072 (KANEGAFUCHI KAGAKU) * claim 1 * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08G C08J C08L C08K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 28 SEPTEMBER 1992	Examiner O'SULLIVAN T.P.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- A : member of the same patent family, corresponding document	